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"QUADRATIC JAHN-TELLER COUPLING IN OCTAHEDRAL SYSTEMS"

by

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In this paper Jahn-Teller vibronic coupling calculations are presented for the general case [$\Gamma_{8g} \times e_g$] in O_h symmetry. The Hamiltonian employed is complete up to terms quadratic in vibrational coordinates q_θ and q_ϵ which

gamma (theta) (epsilon)

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span the $\nu_2(e_g)$ mode of MF_6 systems. Calculational details are discussed. It is concluded that, in agreement with previously reported spectroscopic data for ReF_6 and IrF_6, quadratic terms in the vibronic interaction are essential (both qualitatively and quantitatively) to the complete understanding of intrastate vibronic coupling in transition metal hexafluorides.

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I. INTRODUCTION

Recent experimental studies of transition metal hexafluorides[1-3] have indicated that the spectroscopically observed dynamic Jahn-Teller (JT) effects are not adequately explained by the usual linear JT theory[4]; quadratic terms, at least, are required in the vibronic Hamiltonian. In order to treat hexafluoride data quantitatively, it would be desirable to solve the problem of two JT-active vibrations (ν_2 (e_g) and ν_5 (t_{2g})) vibronically coupled to a Γ_{8g} electronic state for a Hamiltonian complete up to quadratic terms $[\Gamma_{8g} \times (e_g + t_{2g})]_{QUAD}$. Unfortunately, however, the requisite numerical methods are not feasible given currently available computers. In fact, even the $[\Gamma_{8g} \times t_{2g}]_{QUAD}$ problem alone presents an arduous task. The $[\Gamma_{8g} \times e_g]_{QUAD}$ coupling problem is, however, readily soluble. Its solution is presented here and is found to generate a qualitative insight into the nature of the quadratic portion of the JT interaction.

Previous work on $[\Gamma_{8g} \times e_g]_{QUAD}$ (or the very closely related problem: $[E_g \times e_g]_{QUAD}$)[4] has focused on the weak coupling limit[5] or on the case for which linear coupling is large.[6] In the present work matrix elements are given which allow full secular matrices for $[\Gamma_{8g} \times e_g]_{QUAD}$ to be set up and diagonalized numerically. Given a sufficiently large enough truncated secular matrix, accurate eigenvalues and eigenvectors can be obtained for any values of the linear and quadratic parameters. These secular matrices are also applicable to the $[E_g \times e_g]_{QUAD}$ situation.

II. THEORY

The first step toward obtaining the necessary matrix elements for $[\Gamma_{8g} \times e_g]_{QUAD}$ is to find the vibronic Hamiltonian. Englman[4] has discussed in detail the group theoretical techniques which allow a parametric Hamiltonian to be obtained; it is given here with only minor modifications:

$$\underline{\hat{\mathcal{H}}} = \underline{\hat{\mathcal{H}}}^{(0)} + \underline{\hat{\mathcal{H}}}^{(1)} + \underline{\hat{\mathcal{H}}}^{(2)}(a_{1g}) + \underline{\hat{\mathcal{H}}}^{(2)}(e_g) + \ldots \tag{1}$$

in which

$$\underline{\hat{\mathcal{H}}}^{(0)} = \left\{\frac{1}{2}\left(\hat{P}_\theta^2 + \hat{P}_\epsilon^2\right) + \frac{k_\epsilon}{2}\left(q_\theta^2 + q_\epsilon^2\right)\right\}\underline{I}\ , \tag{2}$$

$$\underline{\hat{\mathcal{H}}}^{(1)} = \ell_\epsilon\left(q_\theta\,\underline{\rho_1} + q_\epsilon\,\underline{\rho_2}\right), \tag{3}$$

$$\underline{\hat{\mathcal{H}}}^{(2)}(a_{1g}) = \frac{C_a}{2}\left(q_\theta^2 + q_\epsilon^2\right)\underline{I}\ , \tag{4}$$

and

$$\underline{\hat{\mathcal{H}}}^{(2)}(e_g) = C_\epsilon\left\{\left(q_\theta^2 - q_\epsilon^2\right)\underline{\rho_1} - 2q_\theta q_\epsilon\,\underline{\rho_2}\right\}. \tag{5}$$

(q_θ, q_ϵ) are the mass-weighted normal coordinates of the e_g vibration, $(\hat{P}_\theta, \hat{P}_\epsilon)$ are the conjugate mass-weighted momenta, k_ϵ is the vibrational force constant, $\underline{I}$ is the 4 x 4 identity matrix, $(\ell_\epsilon, C_a, C_\epsilon)$ are the linear and quadratic coupling parameters, and $(\underline{\rho_1}, \underline{\rho_2}, \underline{\rho_3})$ are Dirac matrices.[4] In the following discussion we will also make use of $\underline{\sigma_1}$, $\underline{\sigma_2}$, $\underline{\sigma_3}$, which are additional Dirac matrices as given in reference 4.

Choice of vibronic basis set is important since many matrix elements need to be calculated. In any case, the basis will involve two-dimensional harmonic oscillator functions, $\{X(n_2,\ell_2)\}$ and vectors which represent the four electronic components $\{\vec{V}(\rho_3, \sigma_3)\}$. The $\{\vec{V}(\rho_3,\sigma_3)\}$ are eigenvectors of both $\underline{\rho_3}$ and $\underline{\sigma_3}$ with eigenvalues $\rho_3 = \pm 1$ and $\sigma_3 = \pm 1$. The question of how to combine these factors into a vibronic basis set that is most convenient is now addressed.

One approach, which will only be outlined, involves utilizing molecular point group theory. The vibrational factors, however, do not transform as standard irreducible representations of O_h^* but appropriate linear combinations of these functions can be generated which do so transform. The symmetrized vibrational factors and the electronic factors, which transform as Γ_{8g}, can be combined using Clebsh-Gordon coefficients to give vibronic functions which transform as Γ_{6g}, Γ_{7g}, or Γ_{8g}. Separate secular matrices can then be formed in the usual fashion. This method will not be used, however, because the calculation of matrix elements within this basis set is more cumbersome than need be.

An alternate approach is to use the same vibronic basis that is used in the linear problem. These are written as follows:

$$\vec{b}\,(n_2, \ell_2; \rho_3, \sigma_3; J_2) = X(n_2,\ell_2)\,\vec{V}\,(\rho_3, \sigma_3) \tag{6}$$

in which

$$J_2 = \ell_2 + \frac{\rho_3}{2} = \pm 1/2,\ \pm 3/2, \ldots$$

$$n_2 = 0, 1, 2, \ldots;\ \ell_2 = -n_2, -n_2 + 2, \ldots, n_2$$

$$\rho_3 = \pm 1,\ \sigma_3 = \pm 1.$$

In linear coupling, J_2 is a good quantum number and separate secular matrices are generated for each value of J_2. Upon introduction of quadratic terms ($\underline{\hat{\mathcal{H}}}^{(2)}(e_g)$ in particular), J_2 ceases to be a good quantum number. One can determine, by examining a general matrix element, that $\{2J_2 \bmod 3\}$ remains a good quantum number. Therefore, the following three sets of basis vectors, labeled by J_2, are coupled by the quadratic terms:

$\{\pm 3/2, \pm 9/2, \pm 15/2 \ldots\}^{(0 \bmod 3)}$,

$\{\ldots, -5/2, +1/2, +7/2, \ldots\}^{(1 \bmod 3)}$,

$\{\ldots, -7/2, -1/2, +5/2, \ldots\}^{(2 \bmod 3)}$.

It is of interest to correlate the $\{2\ J_2 \bmod 3\}$ quantum number with irreducible representations of O_h^*. It can be shown that $\{0 \bmod 3\}$ correlates with Γ_{6g} and Γ_{7g} while both $\{1 \bmod 3\}$ and $\{2 \bmod 3\}$ correlate with Γ_{8g}. Thus, one disadvantage of this basis set is that the $\{0 \bmod 3\}$ block is not factored as much as possible (separate Γ_{6g} and Γ_{7g} sets); nonetheless, with modern computers and diagonalization routines, this is not a serious drawback.

The main task remaining is to find integrals of powers of vibrational coordinates over harmonic oscillator functions; these are often referred to as the primitive matrix elements. General formulae exist[7] which allow these matrix elements to be evaluated simply.

Primitive matrix elements relevant to the case at hand are:

$$\int X^*(n_2, \ell_2) q_{\pm}\ X(n_2 + 1, \ell_2 \mp 1) d\tau = \left\{ \frac{1}{2\alpha} (n_2 \mp \ell_2 + 2) \right\}^{1/2}, \tag{7}$$

$$\int X^*(n_2, \ell_2) q_{\mp}^2\ X(n_2 + 2, \ell_2 \pm 2) d\tau = \frac{1}{2\alpha} \left\{ (n_2 \pm \ell_2 + 2)(n_2 \pm \ell_2 + 4) \right\}^{1/2}, \tag{8}$$

$$\int X^*(n_2, \ell_2) q_{\mp}^2\ X(n_2, \ell_2 \pm 2) d\tau = \frac{1}{2\alpha} \left\{ 4 (n_2 \mp \ell_2)(n_2 \pm \ell_2 + 2) \right\}^{1/2}, \tag{9}$$

$$\int X^*(n_2, \ell_2) q_+ q_- X(n_2 + 2, \ell_2) d\tau = \frac{1}{2\alpha} \left\{ (n_2 - \ell_2 + 2)(n_2 + \ell_2 + 2) \right\}^{1/2}, \tag{10}$$

$$\int X^*(n_2, \ell_2) q_+ q_- X(n_2, \ell_2) d\tau = \frac{1}{2\alpha} \{2n_2 + 2\}, \tag{11}$$

in which

$$q_{\pm} = q_\theta \pm i q_\varepsilon$$

$$\alpha = \frac{\omega_\varepsilon}{\hbar} = \frac{k_\varepsilon^{1/2}}{\hbar}.$$

The desired vibronic matrix elements are then readily found:

$$\int \vec{b}^{\dagger}(n_2, \ell_2; \rho_3, \sigma_3; J_2) \frac{\hat{\mathcal{H}}^{(1)}}{\hbar\omega_\varepsilon} \vec{b}(n_2 + 1, \ell_2 + \rho_3; -\rho_3, \sigma_3; J_2) d\tau =$$

$$\{D_2(n_2 + \rho_3\ell_2 + 2)\}^{1/2}, \tag{12}$$

$$\int \vec{b}^{\dagger}(n_2, \ell_2; \rho_3, \sigma_3; J_2) \frac{\hat{\mathcal{H}}^{(2)}}{\hbar\omega_\varepsilon}(a_{1g}) \vec{b}(n_2, \ell_2; \rho_3, \sigma_3; J_2) d\tau = \frac{Q_2[a_{1g}]}{2}\{n_2 + 1\}, \tag{13}$$

$$\int \vec{b}^{\dagger}(n_2, \ell_2; \rho_3, \sigma_3; J_2) \frac{\hat{\mathcal{H}}^{(2)}}{\hbar\omega_\varepsilon}(a_{1g}) \vec{b}(n_2 + 2, \ell_2; \rho_3, \sigma_3; J_2) d\tau =$$

$$\frac{Q_2[a_{1g}]}{4}\{(n_2 + \ell_2 + 2)(n_2 - \ell_2 + 2)\}^{1/2}, \tag{14}$$

$$\int \vec{b}^{\dagger}(n_2, \ell_2; \rho_3, \sigma_3; J_2) \frac{\hat{\mathcal{H}}^{(2)}}{\hbar\omega_\varepsilon}(e_g) \vec{b}(n_2, \ell_2 - 2\rho_3; -\rho_3, \sigma_3; J_2 - 3\rho_3) d\tau =$$

$$Q_2[e_g]\{4(n_2 + \rho_3\ell_2)(n_2 - \rho_3\ell_2 + 2)\}^{1/2}, \tag{15}$$

$$\int \vec{b}^{\dagger}(n_2, \ell_2; \rho_3, \sigma_3; J_2) \frac{\hat{\mathcal{H}}^{(2)}}{\hbar\omega_\varepsilon}(e_g) \vec{b}(n_2 + 2, \ell_2 - 2\rho_3; -\rho_3, \sigma_3; J_2 - 3\rho_3) d\tau =$$

$$Q_2[e_g]\{(n_2 - \rho_3\ell_2 + 2)(n_2 - \rho_3\ell_2 + 4)\}^{1/2}, \tag{16}$$

in which the dimensionless coupling parameters are defined as: $D_2 = \frac{\ell_\varepsilon^2}{2\hbar\omega_\varepsilon^3}$,

$Q_2[a_{1g}] = \frac{C_a}{k_\varepsilon}$, $Q_2[e_g] = \frac{C_\varepsilon}{2k_\varepsilon}$.

Note that σ_3 does not appear on the right hand side of any of these equations and thus two identical secular matrices are generated, one for each value (± 1) of the quantum number σ_3. It will prove to be interesting, for later considerations (see Section III), to use perturbation theory to find the splitting of the $n_2 = 1$ level due to $\hat{\mathcal{H}}^{(2)}(e_g)$ in the unrealistic case of $D_2 = 0$ (no linear coupling). The secular determinant which results from a first order degenerate perturbation theory treatment of the $n_2 = 1$ level, employing equation 15, is

$$\begin{vmatrix} (2 - \lambda) & 4\, Q_2[e_g] \\ 4Q_2[e_g] & (2 - \lambda) \end{vmatrix} = 0 \qquad (17)$$

with solutions

$$\lambda = 2 \pm 4\, Q_2[e_g].$$

These quantities are measured in units of vibrational energy, $\hbar\omega_\varepsilon$. It is possible to obtain a first order expression for $\hat{\mathcal{H}}^{(2)}(a_{1g})$ also; however, this is not necessary since an exact expression easily obtains:

$$\lambda = (n_\varepsilon + 1)\sqrt{1 + Q_2[a_{1g}]} = (n_\varepsilon + 1)(1 + \frac{Q_2[a_{1g}]}{2} + \ldots) . \qquad (18)$$

III. DISCUSSION

Examples of the secular matrix calculation of energy levels of $[\Gamma_8 \times e_g]_{QUAD}$ are given in Figures 1 and 2. The secular matrix used in these calculations was truncated after $n_2 = 10$; a basis of this size results in 44 x 44 matrices for both the {0 mod 3} and {1 mod 3} blocks (the {2 mod 3} block gives the same eigenvalues as {1 mod 3}). Under these circumstances it is required that D_2 be less than 1 for an accurate description of the levels. The upper limit of $Q_2[e_g]$ was not numerically determined, but is probably about 0.5. The behavior of the levels at these large values of D_2 and $Q_2\,[e_g]$ is quite complicated due to specific level repulsions.

D_2 may be taken as positive since the relevant matrix elements are all off-diagonal (Eqn. 12). The situation with respect to $Q_2\,[e_g]$ is more complicated even though it too has all off-diagonal matrix elements in the employed linear JT basis (Eqn. 15, 16). $\hat{\mathcal{H}}^{(2)}\,(e_g)$ will have diagonal matrix elements in a symmetry adapted basis set. The eigenvalues of $\hat{\mathcal{H}}^{(2)}\,(e_g)$ are independent of the sign of $Q_2\,[e_g]$, however, the concomitant changes in the eigenvectors upon changing the sign of $Q_2\,[e_g]$ may alter their symmetry transformation properties. For $Q_2\,[e_g] \rightarrow -\,Q_2\,[e_g]$, $\Gamma_6 \rightarrow \Gamma_7$ and $\Gamma_7 \rightarrow \Gamma_6$.

Several general observations can be made based on these calculations:

i) For the case $D_2 = 0$ (Figure 1), the perturbation expression Eq. 17 is found to be useful over a large range of $Q_2[e_g]$ values ($Q_2[e_g] \lesssim 0.1$) by direct comparison with results of the truncated secular equation calculation. This situation arises because $\hat{\mathcal{H}}^{(2)}(e_g)$ couples n_2 and $n_2 \pm 2$ levels, but not n_2 and $n_2 \pm 1$, as in the linear case.

ii) In the regime ($D_2 < 0.2$, $Q_2[e_g] \lesssim 0.05$), for the $n_2 = 1$ levels, effects of linear and quadratic terms are found to be approximately independent; that is, the ($n_2 = 1$, $J_2 = 1/2$) level is not shifted appreciably as $Q_2[e_g]$ increases, center-of-gravity of the ($n_2 = 1$, $J_2 = 3/2$) levels is preserved, and splitting of ($n_2 = 1$, $J_2 = 3/2$) is approximately the same as in the $D_2 = 0$ case.

iii) Behavior of the $n_2 = 2$ levels are, however, qualitatively different from those of $n_2 = 1$ (see Figures 1 and 2); one difference is in the behavior of the ($n_2 = 2$, $J = 3/2$) levels (Figure 1). For $D_2 = 0$, these levels do not split under $\hat{\mathcal{H}}^{(2)}(e_g)$, whereas $D_2 \neq 0$ allows admixture of $n_2 = 1,3,\ldots$ levels, thus causing ($n_2 = 2$, $J_2 = 3/2$) to split. It should be noted that existing perturbative treatments of $\hat{\mathcal{H}}$ are not able to generate this splitting,[5] although a more complete perturbation calculation would, of course, reproduce these results.

Based on the form of the perturbation energy expressions for the linear and quadratic JT terms, it can be seen that certain n_2 levels are split by $\hat{\mathcal{H}}^{(2)}(e_g)$ in the first order of perturbation theory (*e.g.,* Eq. 17) while the same n_2 levels are split by $\ddot{\mathcal{H}}^{(1)}$ only in the second order.[8] It is thus possible for quadratic JT terms to be more effective at splitting vibronic levels than are linear JT terms. Examination of the perturbation expressions for the $n_2 = 1$ levels verifies this idea:

$$
\begin{aligned}
&\lambda\,(\hat{\mathcal{H}}^{(1)}) = 2 \pm 2(D_2^{\frac{1}{2}})^2 \\
&\lambda\,(\hat{\mathcal{H}}^{(2)}(e_g)) = 2 \pm 4Q_2[e_g]. \qquad (19)
\end{aligned}
$$

$D_2^{\frac{1}{2}}$ is used for comparison with $Q_2[e_g]$ since it is proportional to ℓ_ε just as $Q_2[e_g]$ is proportional to C_ε. Thus, for $D_2^{\frac{1}{2}} = Q_2[e_g] = 0.1$, Eqs. 19 show that the splitting induced by $\hat{\mathcal{H}}^{(2)}(e_g)$ is an order of magnitude more than that induced by $\hat{\mathcal{H}}^{(1)}$. Similar results obtain for $\hat{\mathcal{H}}^{(2)}(a_{1g})$ (see Eq. 18).

Available hexafluoride data[1-3] show that the splitting induced by the linear terms is of the same order of magnitude as the quadratically-induced splittings and shifts. Although these data indicate the expansion of $\underline{\hat{\mathcal{H}}}$ in powers of q_θ and q_ϵ is not converging as rapidly as might be desired, the entire effect cannot be attributed to non-linearity of $\underline{\hat{\mathcal{H}}}$. Greater effectiveness of $\underline{\hat{\mathcal{H}}}^{(2)}(e_g)$ and $\underline{\hat{\mathcal{H}}}^{(2)}(a_{1g})$ in causing shifts and splittings is also an important consideration.

IV. CONCLUSION

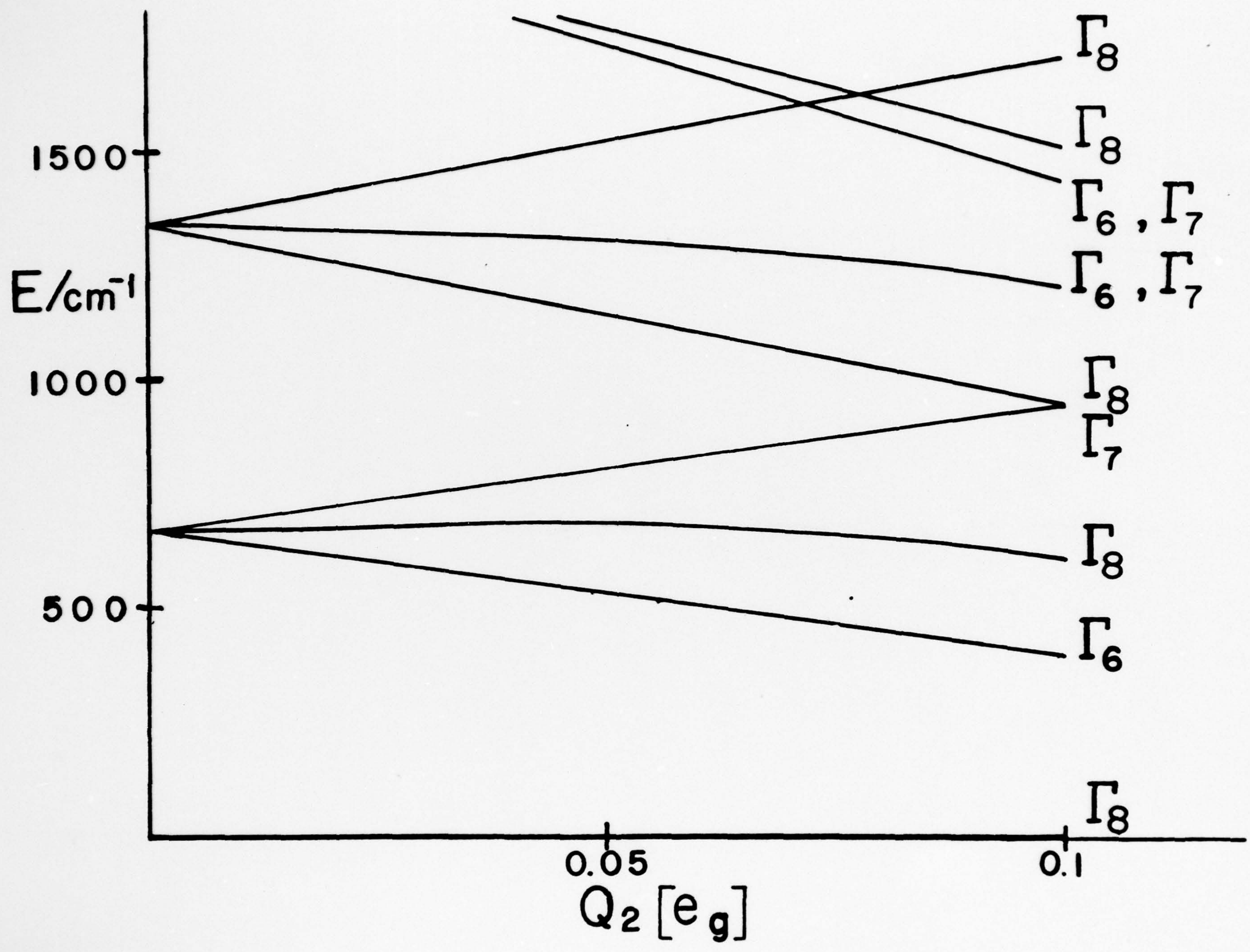
An accurate numerical method is given for treating vibronic coupling of Γ_{8g} (O_h^*) electronic state to an e_g vibration for a vibronic Hamiltonian with linear and quadratic terms. Examples of the calculation are given and general comments on the behavior of the levels under the influence of quadratic terms are made. It is also found that the quadratic coupling term is a more effective perturbation than the linear coupling term with respect to the observed spectroscopic splitting.

REFERENCES

1. G. R. Meredith, J. D. Webb and E. R. Bernstein, Mol. Phys. 34, 995 (1977).
2. E. R. Bernstein and J. D. Webb, Mol. Phys. __, (1978).
3. E. R. Bernstein and J. D. Webb, Mol. Phys. __, (1978).
4. R. Englman, "The Jahn-Teller Effect in Molecules and Crystals," (Wiley-Interscience, New York, 1972).
5. B. Weinstock and G. L. Goodman, Adv. Chem. Phys. 9, 169 (1965).
6. M. C. M. O'Brien, Proc. Roy. Soc. A 281, 323 (1964).
7. C. DiLauro, J. Mol. Spec. 41, 598 (1972).
8. W. Moffitt and W. Thorson, Phys. Rev. 108, 1251 (1957).

Figure 1.

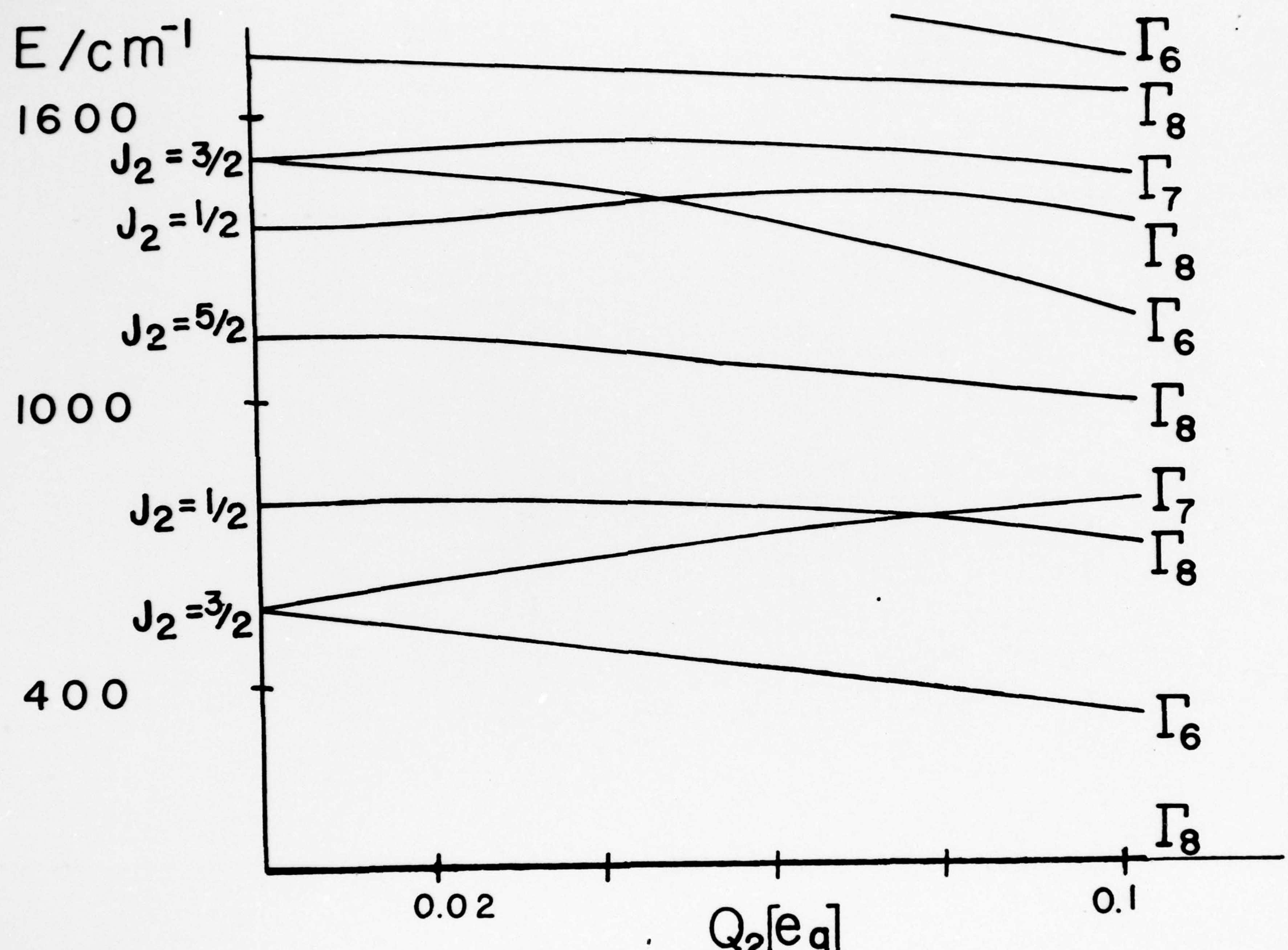
Quadratic Jahn-Teller calculation for coupling of a Γ_8 electronic state with a $\nu_2(e_g)$ vibration, $(\Gamma_8 \times e_g)_{QUAD}$. The fixed parameter values are $D_2 = 0$ and $\nu_2^o = 670\ cm^{-1}$. D_2 is the linear Jahn-Teller coupling parameter and ν_2^o is the unperturbed ν_2 harmonic oscillator frequency. $Q_2\ [e_g]$ is the quadratic coupling parameter. Note the large range over which the splitting is linear in $Q_2\ [e_g]$. In the method employed here, Γ_6 and Γ_7 levels both arise from the same secular matrix (the {0 mod 3} block, see text). The symmetry labels of the eigenvectors are generated from their transformation properties. Changing the sign of $Q_2\ [e_g]$ will not alter the energies, but will interchange Γ_6 and Γ_7 symmetry labels.



Γ_8
Γ_8
Γ_6 , Γ_7
Γ_6 , Γ_7
Γ_8
Γ_7
Γ_8
Γ_6
Γ_8
1500
1000
500
E/cm^{-1}
0.05
0.1
Q_2 [e_g]

Figure 2.

Similar to Figure 1 but D_2 has been set to 0.125. Note that the $n_2 = 1$ for this value of D_2 levels behave similarly to those for which $D_2 = 0$ in that one pair of levels splits symmetrically and the other level remains largely uneffected as Q_2 $[e_g]$ varies. This situation does not hold, however, for the $n_2 = 2$ levels. The J_2 quantum number, which is good at $Q_2[e_g] = 0$, is indicated.


E/cm-1
1600
1000
400
J2 = 3/2
J2 = 1/2
J2 = 5/2
J2 = 1/2
J2 = 3/2
Γ6
Γ8
Γ7
Γ8
Γ6
Γ8
Γ7
Γ8
Γ6
Γ8
0.02
0.1
Q2[eg]

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